



# Process effect of microalgal-carbon dioxide fixation and biomass production: A review

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## ABSTRACT

Global warming caused by anthropogenic CO<sub>2</sub> emission has been one of the most important issues in the fields of science, environment and even international economics and politics. To control and reduce CO<sub>2</sub> emissions, intensive carbon dioxide capture and storage (CCS) technologies have been comprehensively developed for sequestration of CO<sub>2</sub> especially from combustion flue gas.

Microalgae-based CO<sub>2</sub> biological fixation is regarded as a potential way to not only reduce CO<sub>2</sub> emission but also achieve energy utilization of microalgal biomass. However, in this approach culture process of microalgae plays an important role as it is directly related to the mechanism of microalgal-CO<sub>2</sub> fixation and characteristics of microalgal biomass production. The aim of this work is to present a state-of-the-art review on the process effect, especially on the effects of photobiochemical process, microalgal species, physicochemical process and hydrodynamic process on the performance of microalgal-CO<sub>2</sub> fixation and biomass production. Also, the perspectives are proposed in order to provide a positive reference on developing its fundamental research and key technology.

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## Contents

1. Introduction	122
2. Photobiochemical principle and process	122
2.1. CO <sub>2</sub> concentrating mechanism (CCM) process	122
2.2. Photosynthesis process	122
3. Effects of microalgal species	123
4. Effects of physicochemical process	123
4.1. CO <sub>2</sub> concentration	123
4.2. Toxic pollutants in combustion flue gas	126
4.2.1. SO <sub>2</sub>	126
4.2.2. NO <sub>x</sub>	126
4.2.3. Mercury	126
4.3. Initial biomass concentration	126
4.4. Culture temperature	127
4.5. Light	127
4.6. Nutrients	127
4.7. pH value	128
5. Effects of hydrodynamic process	128
5.1. Flow and mixing	128
5.2. Mass transfer	128
6. Process improvement and application	129
7. Conclusions and prospects	129
Acknowledgments	130
References	130

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## 1. Introduction

Carbon dioxide ( $\text{CO}_2$ ) has been regarded as one of the most important greenhouse gases (GHGs). Anthropogenic  $\text{CO}_2$  emissions from fossil fuel utilization especially from coal combustion make a significant contribution to global warming [1]. It has become an important issue in the fields of science, environment and even international economics and politics in recent years.

To effectively reduce the post-combustion  $\text{CO}_2$  emission, the stable, safe and environmentally acceptable post-combustion  $\text{CO}_2$  capture technologies are necessary in addition to improving energy efficiency and developing renewable energies. According to the capture mechanism, post-combustion  $\text{CO}_2$  capture methods can be roughly categorized as chemical absorption, physicochemical adsorption, membrane, cryogenics, chemical looping combustion (CLC) and biotechnology (e.g., terrestrial vegetations or hydroponic algae). From a technical point of view all of these methods are feasible in spite of the differences in capture efficiency and capture capability. However, from an economical point of view, some of the physical and chemical methods mentioned above have to face serious challenges such as high energy consumption for regeneration (e.g. amine), large space requirements and difficult resource-ization for products. Moreover, from an environment-friendly point of view deep oceanic or geological storages may have the venture for  $\text{CO}_2$  leakage over long time [2].

Biologic fixation via microalgae has been regarded as a potential and promising new method for post-combustion  $\text{CO}_2$  capture and storage [3,4]. Fig. 1 shows a flowchart for a microalgal- $\text{CO}_2$  fixation and biomass production system. Biological fixation and storage of  $\text{CO}_2$  via microalgae are essentially photosynthesis, which can convert water and  $\text{CO}_2$  into organic compounds without additional or extra energy consumption and without secondary pollution. Compared with other carbon capture and storage (CCS) methods, microalgal- $\text{CO}_2$  fixation has a lot of advantages, such as wide distribution, high photosynthesis rate, fast growth rate, good environment adaptability and low cost of operation. As an extra benefit, microalgal biomass for energy use is produced after the  $\text{CO}_2$  capture by microalgae.

In the microalgal- $\text{CO}_2$  fixation technology, performances of microalgal- $\text{CO}_2$  fixation and biomass production heavily depend on the culture process conditions, e.g., microalgal growth under combustion flue gas conditions is usually more complex than those under the conditions of the atmospheric environment. Besides microalgal species, the factors influencing microalgal- $\text{CO}_2$  fixation usually include physicochemical parameters (e.g.,  $\text{CO}_2$  concentration, toxic pollutants in combustion flue gas, initial inoculation density, culture temperature, light, nutrients and pH) and hydrodynamic parameters (e.g., parameters of flow, mixing and mass transfer, etc.). Although microalgal- $\text{CO}_2$  fixation and biomass conversion is becoming a research focus, most researches particularly concerned about

carbon fixation strategy, photobioreactor design, conversion technology from microalgal biomass to bioenergy [5–16] and technique-economic evaluation for microalgal energy [17,18]. A completed and systematical review regarding the effect of process characteristics especially in the complex flue gas environment has not yet been reported up to now.

This work attempts to summary and review the state-of-the-art advances on microalgal- $\text{CO}_2$  fixation and biomass production, particularly focusing on the principle and process of carbon fixation, and the effect of microalgal species, physicochemical process parameters and hydrodynamic process parameters on microalgal- $\text{CO}_2$  fixation and biomass production. The challenges and prospects are also discussed.

## 2. Photobiocchemical principle and process

### 2.1. $\text{CO}_2$ concentrating mechanism (CCM) process

As similar as other photosynthetic organism, microalgae concentrate or store  $\text{CO}_2$  through a Calvin–Benson cycle, a redox reaction, in which the photosynthesis needs to be supplied with both a source of energy to drive this process, and the electrons to convert carbon dioxide into a carbohydrate. Especially for unicellular microalgae,  $\text{CO}_2$  concentrating mechanism (CCM) plays a vital role during carbon fixation process as it can enhance the level of  $\text{CO}_2$  at the active site of ribulose biphosphate carboxylase-oxygenase (Rubisco) by transporting inorganic carbon or carbon dioxide into the cell. CCM directly results in the increase of photosynthetic rate and the decrease of the photorespiration [19–21].

A typical CCM process in microalgae can be illustrated in Fig. 2 (a), although there are a few differences in CCM for different typical microalgae such as *Cyanobacteria*, *Chlorophyta* and red *chromist* algae. [22]. Usually, dissolved inorganic carbon (DIC) exists in water in the form of  $\text{CO}_2$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$  and  $\text{H}_2\text{CO}_3$  when the dynamic ionization equilibrium is reached, but only  $\text{CO}_2$  and  $\text{HCO}_3^-$  are the main DIC forms which can be used by microalgal cells in different ways. For instance, both  $\text{HCO}_3^-$  and  $\text{CO}_2$  can be simultaneously used by most of microalgae [23,24].  $\text{HCO}_3^-$  has been demonstrated to be used not only via a direct way, e.g., active transport [25,26] and cation exchange [27,28], but also via an indirect way which catalyzes  $\text{HCO}_3^-$  as  $\text{CO}_2$  and  $\text{OH}^-$  by periplasmic carbonicanhydrase (pCA) [29–33]. However, there is an exception that only  $\text{CO}_2$  can be used by some microalgae [34,35].

During the process of DIC conversion, Carbonic anhydrase (CA) and pyrenoid play the vital role in microalgal CCM. CA includes Periplasmic Carbonic anhydrase (pCA), Cytosolic Carbonic Anhydrase (cyCA) and chloroplast carbonic anhydrase (chCA). The function of pCA is to keep the balance between  $\text{CO}_2$  and  $\text{HCO}_3^-$  and continuously supply  $\text{CO}_2$  for cells [20,36], and cyCA may accelerate the transport of  $\text{CO}_2$  and  $\text{HCO}_3^-$  from plasma membrane to chloroplasts [23,36]. chCA is considered as the most important CA in CCM. Pyrenoid is also considered to be the other component of the CCM for unicellular green microalgae. Using biochemistry methods it has been found that pyrenoid mainly consisted of Rubisco [37]. Since the anhydrase in microalgal cells are liable to be influenced by the process factors, it can be inferred that these factors actually act on microalgal CCM.

### 2.2. Photosynthesis process

Microalgal photosynthesis is a physicochemical process that converts carbon dioxide into organic compounds using light energy and release molecular oxygen [38]. Frequently, the following empirical equation is used to describe the overall reaction of

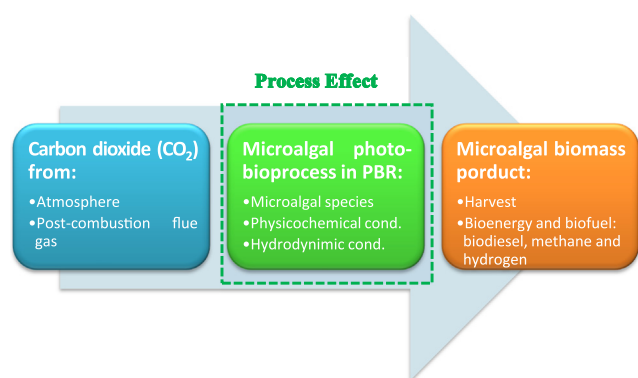


Fig. 1. Flowchart of microalgal- $\text{CO}_2$  fixation and biomass production.

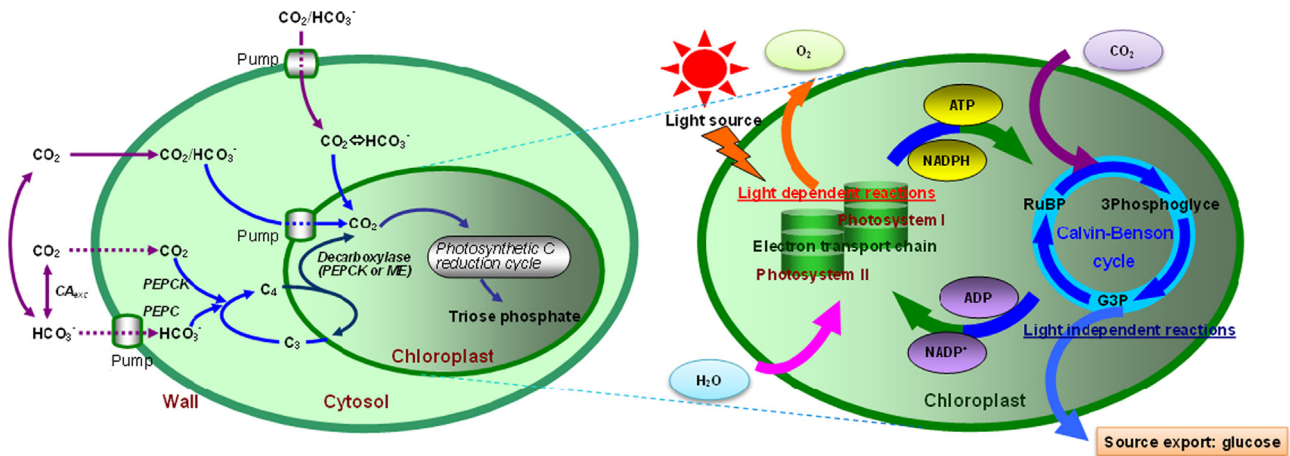
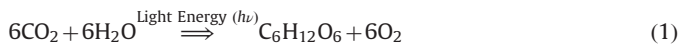


Fig. 2. Photobiochemical principles of microalgal- $\text{CO}_2$  fixation: (left) typical carbon concentrating mechanism [22] and (right) photosynthesis process [40].

photosynthesis:



In this reaction, the standard free energy for the synthesis of glucose is 2870 kJ/mol [39].

Usually, photosynthesis has been regarded to occur in main stages (Fig. 2(b)): light dependent reactions and light independent reactions. The light dependent reactions capture the light energy and convert ADP and  $\text{NADP}^+$  into the energy carriers ATP and NADPH via the electron transport chain and produce oxygen. In this process, Antenna complexes formed by Chlorophyll and other carotenoids transfer light energy to P700 (part of Photosystem I) or P680 (part of Photosystem II), which are the different photochemical reaction centers located on the thylakoid membrane of the chloroplast. Excited electrons are transferred to electron acceptors, leaving the reaction center in an oxidized state [14,40]. Then, the light independent reactions capture carbon dioxide and produce the precursors of carbohydrates using previously formed ATP and NADPH by the Calvin–Benson cycle.

### 3. Effects of microalgal species

Besides the culture conditions microalgal species are most vital as they directly influence the performances carbon fixation and biomass production. Table 1 gives the effect of typical energy-microbial species on the parameters of microalgal growth characteristic, biomass production and carbon fixation. Fig. 3 shows the relationship between microalgal species and maximum biomass production rate as well as maximum  $\text{CO}_2$  fixation rate.

$\text{CO}_2$  fixation and biomass production performances vary with microalgal species, although the data may not have a strict comparability as microalgae have different biological performance and were cultured in different conditions. However, compared with other species (e.g., Cyanophytes and Chrysophyte), Chlorella were observed to have a better performance. The biomass production rate and carbon fixation rates were up to 1.060 g/L/d and 1.992 g/L/d, respectively.

Compared with atmospheric- $\text{CO}_2$  culture process, several harsh conditions such as high  $\text{CO}_2$  concentration, high aeration ratio (aeration load) and toxic pollutants in flue gas have negative impacts on the growth of microalgal species. However, these effects may be overcome for some microalgal species by adaption, making it possible to endure the rigorous flue gas conditions and continue growing [68–73]. Few microalgae were even able to tolerate a high level  $\text{CO}_2$  concentration up to 70% [50,55,74,75] or even 100% [42], high aeration rate of 2.0 vvm [46], low pH value of

less than 3.5 [56] and toxic compounds with 100 ppm  $\text{SO}_2$  and  $\text{NO}_x$  [53]. Additionally, effects of nutrient source, light intensity, culture temperature on microalgal growth are also related to microalgal species. Optimal ranges or values of these parameters to achieve high  $\text{CO}_2$  fixation rates and biomass productions are usually different for each microalgal species.

It is necessary to develop the high performance species to realize the maximization of microalgal  $\text{CO}_2$  fixation and biomass production in more complex and harsh environments. Most of microalgal species are isolated from natural streams, lakes or oceans and pre-adapted for the living environment through artificial domestication, and have been successfully used for fixation of atmospheric  $\text{CO}_2$  [76]. However, unlike atmospheric air with extremely low  $\text{CO}_2$  (about 0.038% v/v), actual post-combustion flue gas has the features of high  $\text{CO}_2$  concentration (10–20% or more v/v), high flow rate, high temperature (80–120 °C or above) and toxic compounds ( $\text{SO}_x$ ,  $\text{NO}_x$  and mercury). It means that the microalgal species will be required to have ability for post-combustion  $\text{CO}_2$  fixation [77–79]. Therefore, selection, isolation and culture of microalgal species with fast growth rate, high photosynthetic rate, strong environmental tolerance/adaptability and high lipid content will be future research and development directions. Moreover, the general microalgal species for industrial application are obtained using natural breeding method. Usually, they do not have outstanding performance. To enhance and improve microalgal- $\text{CO}_2$  fixation and biomass production, it is also important to introduce the high-performance microalgal species using advanced breeding methods such as physicochemical mutation, cellfusion/genetic improvement and crossbreeding [80].

Microalgal- $\text{CO}_2$  biofixation and biomass production is a complex physicochemical process especially in cases of flue gas environment. Therefore, besides microalgal species the process must be influenced by culture parameters including physicochemical and hydrodynamic parameters. To improve the ability of microalgal carbon sequestration and the efficiency of biomass production, it is important to insight into the impacts of these factors and to further optimize these parameters.

### 4. Effects of physicochemical process

#### 4.1. $\text{CO}_2$ concentration

It was demonstrated that the growth performance for some microalgal can be negatively affected when suffering from  $\text{CO}_2$  with higher than 1% (v/v) concentration [57]. However, for other microalgae especially for energy microalgae  $\text{CO}_2$  concentration has a complex effect on microalgal carbon biofixation and biomass

**Table 1**Summary of microalgal biomass production and CO<sub>2</sub> fixation parameters under different process conditions<sup>a</sup>.

Microalgal species <sup>b</sup>	CO <sub>2</sub> (% v/v)	AR (vvm)	ID (g/L)	LI (μmol/m <sup>2</sup> /s)	L/D (h/h)	T (°C)	N (mg/L)	P (mg/L)	pH (–)	PBR <sup>c</sup>	OS <sup>d</sup>	V&S	CM	SGR <sup>e</sup> (1/d)	BPR <sup>f</sup> (g/L/d)	CFR <sup>g</sup> (g/Ld)	Ref.
NS1	15	NA	0.18	168	24/0	25	NA	NA	6.3	RB	Batch	V=1 L	Mf/2	0.700	0.256	0.482	[41]
NS2	15	NA	0.18	168	24/0	25	NA	NA	6.3	RB	Batch	V=1 L	Mf/2	0.657	0.229	0.431	
PT	15	NA	0.18	168	24/0	25	NA	NA	6.3	RB	Batch	V=1 L	Mf/2	0.501	0.180	0.338	
CS T-1	15	0.83	0.002–0.005	110	NA	30–45	NA	NA	NA	SF	Batch	V=0.6 L	Fitzgerald	0.915–3.289	0.009–0.106	0.130	[42]
	0.038–100	0.83	0.03	110	NA	35	NA	NA	4.8–10.7	SF	Batch	V=0.6 L	Fitzgerald	0.542–0.840	0.084–0.394	0.158–0.741	
C A-2	20	NA	NA	500	NA	30–40	12.38	9.19	6.0 (initial)	BF	Batch	V=0.3 L	MC	0.773–2.411	NA	NA	[43]
C H-84	5–40	NA	NA	500	NA	40	12.38	9.19	6.0 (initial)	BF	Batch	V=0.3 L	MC	1.417–1.599	NA	NA	
CL	20	0.2	NA	250	24/0	25	NA	NA	NA	NA	NA	V=4 L	NA	0.078	0.400	0.752	[44]
NOA-113	15	0.036	0.4	174.4	12/12	25	70.00	5.17	<6.0	LT	Batch	V=4 L, D × L=5 × 2500 cm	Mf/2	0.309	0.358	0.674	[45]
CV UTEX259	0.038–20	2	0.1	110	24/0	27	138.61	168.68	7.2–5.4	BC	Batch	V=0.4 L	N-8	0.216–0.385	0.067–0.344	0.063–0.648	[46]
CS HA-1	10	0.3	0.3	51.4	12/12	28	693.07	284.93	6.0 (initial)	HT	Batch	D × L=1.6 × 2700 cm	M4N	0.399	0.569	1.070	[47]
IG(F)	0.038	NA	0.137	115	12/12	18	4-Nitrate	NA	NA	BC	Batch	NA	NA	0.207	0.126	0.236	[48]
	0.038	NA	0.137	115	12/12	18	4-Nitrite	NA	NA	BC	Batch	NA	NA	0.195	0.117	0.220	
	0.038	NA	0.137	115	12/12	18	4-Urea	NA	NA	BC	Batch	NA	NA	0.183	0.100	0.187	
PP1380-1 A	2	0.04	0.075	120	14/10	25	20.00		7.0 (initial)	PST	Batch	V=50 L, D × L=2.4 × 8400 cm	Hemerick	0.250	0.304	0.572	[49]
CS KR-1	10–70	1	0.1	200	24/0	25	693.07	284.93	6.0–3.5	BC	Batch	V=0.2 L, D × H=3.5 × 40 cm	M4N	0.336–0.671	0.108–0.917	0.204–1.723	[50]
IG(P)	0.038	NA	0.001	183.6	24/0	20	12.35	1.29	NA	EF	Batch	V=1.0 L	f/2	0.645	0.011	0.020	[51]
CC	0.038	NA	0.001	183.6	24/0	20	12.35	1.29	NA	EF	Batch	V=1.0 L	f/2	0.387	0.007	0.014	
CV(D)	0.038	0.45	0.45	980	1/10	29	693.07	170.96	6.8 (initial)	BC	Batch	V=3.0 L	DS	0.293	0.436	0.819	[52]
	0.038	0.45	0.25–0.60	980	1/10	29	693.07	170.96	6.8 (initial)	FPA	Batch	V=3.0 L	DS	0.339–0.416	0.543–0.840	1.021–1.579	
CS KR-1	15	0.5	0.1	450	24/0	25	693.07	284.93	5.6–7.2	WB	Batch	V=0.05 L	M4N	1.547	1.400	2.632	[53]
CV(J)	0.038–30	NA	0.02	58.8	NA	25	28.00	6.09	NA	EF	Batch	V=0.1 L	N-8	0.528–0.745	0.092–0.387	0.174–0.727	[54]
C ZY-1	0.038–70	0.25	0.1	140	12/12	25	693.07	284.93	7.0–3.0	BC	Batch	V=1.0 L	M4N	0.347–0.677	0.117–0.950	0.219–1.768	[55]
EG	10	0.03	0.03	480	24/0	28	212.12	227.94	3.5 (initial)	BC	Semi-C	V=100 L, L × W × H=90 × 20 × 70 cm	MC	0.599	0.114	0.214	[56]
CV(C)	0.1–2.8	0.3	1.644	200	12/12	25–30	13.86	2.28	NA	HMF	Cont.	V=10 L, D × H=11 × 110 cm	NA	NA	0.102–1.060	0.192–1.992	[57]
SO	0.038–18	0.3	0.15	44.8	12/12	30	173.27	284.93	7.4–5.3	CF	Batch	V=1.8 L	MC	0.216–0.261	0.064–0.090	0.120–0.169	[58]
CK	0.038–18	0.3	0.15	44.8	12/12	30	34.65	17.10	8.7–6.4	CF	Batch	V=1.8 L	BM	0.199–0.257	0.061–0.090	0.115–0.169	
SS(D)	0.038–12	0.3	0.15	44.8	12/12	30	173.27	284.93	7.08–10.22	BC	Batch-3S	V=3 × 1.8 L, D × H=6.5 × 60 cm	MZarrouk	0.330–0.440	0.040–0.200	0.075–0.376	[59]
SO	0.038–12	0.3	0.15	44.8	12/12	30	173.27	284.93	6.95–10.03	BC	Batch-3S	V=3 × 1.8 L, D × H=6.5 × 60 cm	MC	0.150–0.220	0.040–0.140	0.075–0.263	
CS(C)	0.038–5	0.25	0.011–0.113	300	24/0	26	46.33	4.76	NA	BC	Batch	V=0.8 L, D × H=7 × 30 cm	Mf/2	0.127–0.605	0.074–0.207	0.017–0.389	[60]
AMN	15	1	0.1	150	24/0	35	24.71	7.13	8.0–8.7	BC	Batch	V=2.4 L, D × H=7 × 70 cm	BGN	0.605	0.769	1.446	[61]
	15	1	0.1	150	24/0	35	24.71	7.13	8.0–9.0	AL	Batch	V=2.4 L, D × D <sub>i</sub> × H=7 × 1 × 70 cm	BGN	0.611	0.800	1.504	
AMN	15	1	0.1	150	24/0–2/22	35	24.71	7.13	8	BC	Batch	V=3.0 L, D × H=7.5 × 75 cm	BGN	0.067–0.605	0.008–0.769	0.016–1.446	[62]
CS AG10002	0.5–5	0.1	0.01	100	24/0	20	17.65	0.29	7.2 (initial)	BC	Batch	V=0.6 L, D × H=4.6 × 46 cm	Allen	0.792–0.885	0.192–0.335	0.360–0.630	[63]



	0.5	0.06–0.40	0.01	100	24/0	20	17.65	0.29	7.2 (initial)	BC	Batch	V=0.6 L, D × H=4.6 × 46 cm	Allen	0.879–0.933	0.323–0.448	0.608–0.843	
CV(S)	10	1.06	0.2	68	24/0	22	2.25–123.53	13.36	6.0 (initial)	CF	Batch	V=0.1 L	3N-BBM+V	0.077–0.181	0.033–0.278	0.063–0.522	[64]
	10	1.06	0.1–0.8	68	24/0	22	0.00	13.36	NA	CF	Batch	V=0.1 L	3N-BBM+V	0.051–0.070	0.008–0.083	0.016–0.157	
BB	10	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	0.027	0.050	[65]
CV(Y)	10	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	0.105	0.197	
SS(Y)	10	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	0.218	0.409	
CS WT	2–25	0.05	0.2	300	24/0	25	37.06	3.88	NA	BC	Batch	V=0.8 L, D × H=7 × 30 cm	Mf/2	0.276–0.324	0.142–0.200	0.266–0.376	[66]
CS MTF-7	2–25	0.05	0.2	300	24/0	25	37.06	3.88	NA	BC	Batch	V=0.8 L, D × H=7 × 30 cm	Mf/2	0.312–0.411	0.183–0.358	0.345–0.674	
CS(Z)	10–20	0.2	0.15	84	12/12	18	12.35	1.29	8.0–5.2	BC	Batch	V=1.0 L, D × H=6.5 × 40 cm	f/2	0.297–0.374	0.150–0.271	0.282–0.510	Present work

<sup>a</sup> CO<sub>2</sub>=carbon source, AR=aeration ratio, ID=initial biomass density, LI=light intensity, L/D=light-dark circle, T=temperature, N=Nitrogen source, P=phosphorus source, PBR=photobioreactor, V&S=volume and size; OS=operating strategy, CM=culture medium, SGR=special growth rate of microalgal biomass, BPR=Biomass production rate, CFR=CO<sub>2</sub> fixation rate.

<sup>b</sup> NS1 = *Nannochloris* sp., NS2 = *Nannochloropsis* sp., PT = *Phaeodactylum tricornutum*, CS T-1 = *Chlorella* sp. T-1, C A-2 = *Chlorella* A-2, C H-84 = *Chlorella* H-84, CL = *Chlorococcum littoral*, NOA-113 = NOA-113, CV UTEX259 = *Chlorella vulgaris* UTEX259, CS HA-1 = *Chlorella* sp. HA-1, IG(F) = *Isochrysis galbana*, PP 1380-1A = *Porphyridium purpureum* 1380-1A, CS KR-1 = *Chlorella* sp. KR-1, IG(P) = *Isochrysis galbana*, CC = *Chaetoceros calcitrans*, CV(D) = *Chlorella vulgaris*, CS KR-1 = *Chlorella* sp. KR-1, CV(J) = *Chlorella vulgaris*, C ZY-1 = *Chlorella* ZY-1, EG = *Euglena gracilis*, CV(C) = *Chlorella vulgaris*, SO = *Scenedesmus obliquus*, CK = *Chlorella kessleri*, SS(D) = *Spirulina* sp., SO = *Scenedesmus obliquus*, CS(C) = *Chlorella* sp., AMN = *Aphanothece microscopica* Nägeli, CS AG10002 = *Chlorella* sp. AG10002, CV(S) = *Chlorella vulgaris*, BB = *B. braunii*, CV(Y) = *C. vulgaris*, SS(Y) = *Scenedesmus* sp., CS WT = *Chlorella* sp. WT, CS MTF-7 = *Chlorella* sp. MTF-7, CS(Z) = *Chlorella* sp.

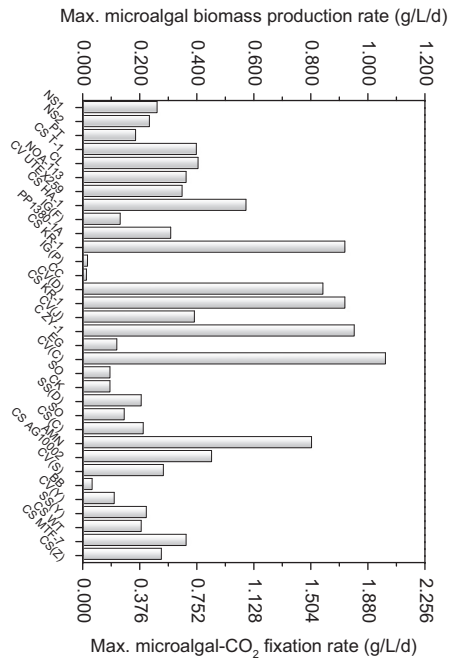
<sup>c</sup> RB=Roux bottles, SF=spinner flask, FB=bubbled flask, LT=long tubular, BC=bubble column, HT=helical tubular, PST=pilot-scale tubular, EF=Erlenmeyer flasks, FPA=flat plate airlift, WB=washing bottle, CF=conical flask, T=tubular, HFM=hollow fiber membrane, AL=air-lift.

<sup>d</sup> Batch=batch, Semi-C=semi-continuous, Cont.=continuous, Batch-3S=batch with three stages.

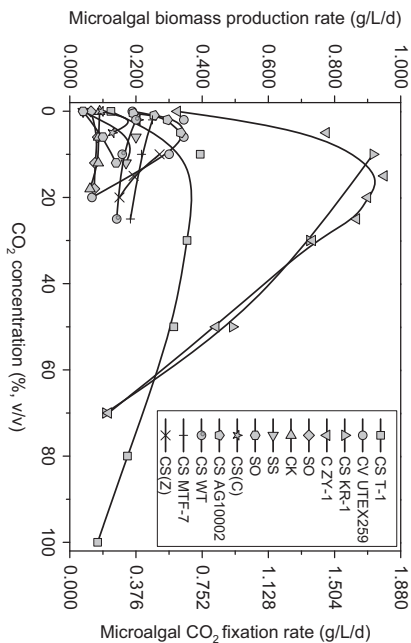
<sup>e</sup> Calculated by  $SGR = (\ln X_t - \ln X_0) / (t - t_0) \times X$  is microalgal biomass concentration (g/L) and  $t$  is time (d).

<sup>f</sup> Calculated by  $BPR = (X_t - X_0) / (t - t_0)$ .

<sup>g</sup> Calculated by  $CFR = 1.88 \times BPR$ , which is obtained based on typical microalgal molecular CO<sub>0.48</sub>H<sub>1.83</sub>N<sub>0.11</sub>P<sub>0.01</sub> [67,14].



**Fig. 3.** Relationship between microalgal species and its maximum microalgal-CO<sub>2</sub> fixation rate as well as biomass production rate under different process conditions.



**Fig. 4.** Effect of CO<sub>2</sub> concentration on microalgal-CO<sub>2</sub> fixation and biomass production. NS1 = *Nannochloris* sp., NS2 = *Nannochloropsis* sp., PT = *Phaeodactylum tricornutum*, CS T-1 = *Chlorella* sp. T-1, C A-2 = *Chlorella* A-2, C H-84 = *Chlorella* H-84, CL = *Chlorococcum littoral*, NOA-113 = NOA-113, CV UTEX259 = *Chlorella vulgaris* UTEX259, CS HA-1 = *Chlorella* sp. HA-1, IG(F) = *Isochrysis galbana*, PP 1380-1A = *Porphyridium purpureum* 1380-1A, CS KR-1 = *Chlorella* sp. KR-1, IG(P) = *Isochrysis galbana*, CC = *Chaetoceros calcitrans*, CV(D) = *Chlorella vulgaris*, CS KR-1 = *Chlorella* sp. KR-1, CV(J) = *Chlorella vulgaris*, C ZY-1 = *Chlorella* ZY-1, EG = *Euglena gracilis*, CV(C) = *Chlorella vulgaris*, SO = *Scenedesmus obliquus*, CK = *Chlorella kessleri*, SS(D) = *Spirulina* sp., SO = *Scenedesmus obliquus*, CS(C) = *Chlorella* sp., AMN = *Aphanothece microscopica* Nägeli, CS AG10002 = *Chlorella* sp. AG10002, CV(S) = *Chlorella vulgaris*, BB = *B. braunii*, CV(Y) = *C. vulgaris*, SS(Y) = *Scenedesmus* sp., CS WT = *Chlorella* sp. WT, CS MTF-7 = *Chlorella* sp. MTF-7, CS(Z) = *Chlorella* sp.

production performances (Fig. 4). Most of microalgae grow only at low CO<sub>2</sub> concentrations level, and would be inhibited when CO<sub>2</sub> concentration level was higher than 5% (v/v) [81,82]. Some microalgae can grow under higher flue gas-CO<sub>2</sub> concentrations level (10–15%), but the carbon fixation and biomass production rate are less than that under lower CO<sub>2</sub> concentration. Very few microalgal species are able to tolerate extremely high CO<sub>2</sub> level up to 70% (e.g., CS KR-1 and C ZY-1) and even 100% (e.g., CS T-1). Essentially, microalgal growth and its CO<sub>2</sub> fixation are strongly related to CCM [83]. High concentrations of CO<sub>2</sub> (even more than 1% v/v) significantly inhibited CA activity and CCM microalgal cell formation has a significantly negative effect on activity of CA. When increasing CO<sub>2</sub> concentration the hydrolysis of CO<sub>2</sub> moves to the direction of the positive reaction, resulting in the increase of HCO<sub>3</sub><sup>-</sup> and H<sup>+</sup> concentration which decrease the pH value in the medium. Low pH value may inhibit the activity of carbonic anhydrase (CA), which plays an important catalytic role in inter-change between CO<sub>2</sub> and HCO<sub>3</sub><sup>-</sup> and is regarded as an important

factor of CCM. As a result, the microalgal performance on carbon biofixation is weakened.

However, according to the analysis of effects of CO<sub>2</sub> concentration on cellular morphology, photosynthetic physiology and molecular biology (e.g. cell vacuoles, CA and RuBisCO), when the increase of CO<sub>2</sub> concentration gives rise to the decreases of the pH value in the medium, some microalgal cell was able to adapt to the coercion of high concentration CO<sub>2</sub> [84] through different methods, e.g., gene regulation and increasing the energy allocation proportion PSI/PSII. These methods can temporarily reduce the synthesis of organic carbon and simultaneously provide more ATP to maintain the pH stability inside the cell. This is why they were able to tolerate extremely high CO<sub>2</sub> concentration.

The optimal CO<sub>2</sub> concentration for most microalgal species was usually recommended to be 0.038–10%, e.g., the maximum biomass production was observed at 2.5% CO<sub>2</sub> for microalgae CS(C) [60] while at 6% for SO and CK [58]. Although the optimal CO<sub>2</sub> concentration levels for microalgal growth varied with microalgal species, the effect of CO<sub>2</sub> at lower concentrations was more pronounced than at higher ones [9].

## 4.2. Toxic pollutants in combustion flue gas

### 4.2.1. SO<sub>2</sub>

The presence of SO<sub>2</sub> has a strongly inhibited effect on microalgal growth (Table 2). When SO<sub>2</sub> concentration exceeds 100 ppm, it is almost impossible to grow for most of microalgae [85]. Some

**Table 2**  
Effect of toxic pollutants in flue gas on microalgal-CO<sub>2</sub> fixation and biomass production<sup>a</sup>.

Microalgal species <sup>b</sup>	CO <sub>2</sub> (%) /SO <sub>2</sub> (ppm)/NO (ppm)	SGR (1/d) <sup>c</sup>	BPR (g/L/d) <sup>d</sup>	CFR (g/L/d) <sup>e</sup>	Ref.
NS1	15/0/0	0.700	0.256	0.482	[41]
	15/50/0	0.683	0.245	0.461	
	15/0/300	0.268	0.077	0.146	
NS2	15/0/0	0.657	0.229	0.431	[41]
	15/50/0	0.619	0.207	0.390	
	15/0/300	0.344	0.098	0.184	
CS T-1	15/10/30	0.978	0.368	0.691	[42]
	15/5/15	1.009	0.418	0.785	
	15/20/60	1.050	0.493	0.926	
	15/50/150	NA	NA	NA	
	15/80/240	NA	NA	NA	
NOA-113	15/0/0	0.309	0.358	0.674	[45]
	15/0/100	0.292	0.317	0.595	
	15/0/300	0.288	0.308	0.580	
CS HA-1	10/0/0	0.399	0.569	1.070	[47]
	10/0/100	0.310	0.160	0.301	
CS KR-1	15/0/0	1.547	1.400	2.632	[53]
	15/60/0	1.353	0.889	1.671	
	15/100/0	1.157	0.556	1.044	
	15/150/0	NA	NA	NA	
CS KR-1	15/0/0	1.519	1.311	2.465	[53]
	15/0/100	1.465	1.156	2.172	
	15/0/300	NA	NA	NA	
	10/0/0	0.599	0.114	0.214	
EG	10/5/26	0.636	0.138	0.259	[56]
	23/87/78	0.352	0.242	0.454	
CS WT	23/87/78	0.352	0.242	0.454	[66]
CS MTF-7	23/87/78	0.421	0.383	0.721	[66]

<sup>a</sup> SGR=special growth rate of microalgal biomass, BPR=Biomass production rate, CFR=CO<sub>2</sub> fixation rate.

<sup>b</sup> NS1=*Nannochloris* sp., NS2=*Nannochloropsis* sp., CS T-1=*Chlorella* sp. T-1, NOA-113=NOA-113, CS HA-1=*Chlorella* sp. HA-1, CS KR-1=*Chlorella* sp. KR-1, EG=*Euglena gracilis*, CS WT=*Chlorella* sp. WT, CS MTF-7=*Chlorella* sp. MTF-7.

<sup>c</sup> Calculated by  $SGR = (\ln X_t - \ln X_0) / (t - t_0)$ ,  $X$  is microalgal biomass concentration (g/L) and  $t$  is time (d).

<sup>d</sup> Calculated by  $BPR = (X_t - X_0) / (t - t_0)$ .

<sup>e</sup> Calculated by  $CFR = 1.88 \times BPR$ , which is obtained based on typical microalgal molecular CO<sub>0.48</sub>H<sub>1.83</sub>N<sub>0.11</sub>P<sub>0.01</sub> [67,14].

microalgal species are able to grow difficult in the condition of high SO<sub>2</sub> concentration, but they have a longer lag phase than that without SO<sub>2</sub> presence. With the increase of SO<sub>2</sub> concentration, the inhibited effect can be enhanced, resulting in a sharp reduction in carbon fixation and biomass production, e.g., even *Chlorella* sp. KR-1 which was regarded as a high-performance microalgal species could not survive under the condition of 150 ppm SO<sub>2</sub> with 15% CO<sub>2</sub> [86].

Actually, SO<sub>2</sub> may not directly inhibit the microalgal growth [87]. The inhibition effects of SO<sub>2</sub> on microalgae growth can be essentially attributed to the effect of pH value. The H<sup>+</sup> release produced by hydrolysis of SO<sub>2</sub> cause a reduction in pH of the culture medium [88], thereby indirectly affecting the normal conduct of the CCM and even killing the microalgae cells at last when the pH was below 3.0 [42]. However, if pH of the culture medium is artificially controlled as constant by neutralization method, the microalgal growth characteristic is almost the same without the presence of SO<sub>2</sub> [75]. It seems to indirectly demonstrate that the effect of SO<sub>2</sub> on microalgae is achieved through pH value in the batch strategy. However, this situation is not seen in all occasions. Other investigations indicated that the suppression effect of SO<sub>2</sub> on microalgae is associated not only with pH value (H<sup>+</sup> concentration in the culture medium) but also with SO<sub>4</sub><sup>2-</sup> and HSO<sub>4</sub><sup>-</sup> also from SO<sub>2</sub> hydrolysis, suggesting that SO<sub>4</sub><sup>2-</sup> and HSO<sub>4</sub><sup>-</sup> are inhibition factors of microalgal growth [66].

### 4.2.2. NO<sub>x</sub>

In actual flue gas, the total NO<sub>x</sub> emission level varies from several hundreds to thousands ppm with more than 90–95% NO and 5–10% NO<sub>2</sub>. After flue gas de-NO<sub>x</sub> process the NO still at the level of 50–200 ppm. Unlike water-soluble SO<sub>2</sub> which result in significant decrease of pH in the culture medium, NO is hard to directly impact the growth of microalgae via pH in the culture medium [45]. However, the presence of NO is associated with microalgae cells physiological conditions. Its concentration usually has two-side influence on growth of microalgae. This influence is also closely related to microalgal species. Extremely low concentrations NO may even be absorbed by the culture medium and transformed into NO<sub>2</sub><sup>-</sup> as the source of nitrogen nutrition of microalgae in the process of using inorganic forms [9]. However, this positive influence is quite limited: the increased NO concentration results in at least the decreased growth rate of microalgae for most of microalgal species; NO with higher than 300 ppm may give rise to the decline of microalgae [53] (Table 2).

### 4.2.3. Mercury

As one of the most important trace metals emitted from coal-fired power stations, mercury exists in three primary forms in post-combustion flue gas: elemental mercury (Hg<sup>0</sup>), oxidized mercury (Hg<sup>2+</sup>) and particle-bound mercury (Hg<sub>p</sub>). Usually, Hg<sub>p</sub> can be separated by high-efficiency particle collector such as FF or ESP. Due to its water-indissolubility, Hg<sup>0</sup> often is oxidized to Hg<sup>2+</sup> and then removed by washing methods in many mercury control technologies. Until now the effect of Hg<sup>0</sup> on microalgae was almost not involved at all while Hg<sup>2+</sup> had been experimentally investigated. It is observed that microalgal growth rate can be inhibited even though Hg<sup>2+</sup> concentration was at an extremely low level. Naturally, trace metal ion plays the destructive role on chlorophyll. With the increasing concentration of Hg<sup>2+</sup> the Chlorophyll content decreased gradually, directly causing the reduction of photosynthetic efficiency [89].

## 4.3. Initial biomass concentration

As similar as other microbial growth process, most microalgal growth in batch culture has four different growth stages: lag

phase, exponential or log phase, stationary phase and death phase. Microalgal growth characteristic can be estimated by two models a first-order dynamic model called as “J” curve in the log phase (in this case the microalgal biomass concentration at the end of the lag phase is close to the initial inoculation concentration):

$$dX/dt = \mu X \quad (2a)$$

Or a Logistic model called as “S” curve in the whole phases:

$$dX/dt = \mu_{\max} X(1 - X/X_{\max}) \quad (2b)$$

Theoretically, microalgal biomass production or corresponding carbon fixation increases as the initial inoculation concentration increases under given conditioning factors and culture time. In the microalgal growth process, increase of initial biomass concentration can reduce CO<sub>2</sub> load and enhance the tolerance to CO<sub>2</sub> [60] and even toxic compounds such as SO<sub>2</sub> and NO, leading to increased biomass production [90], e.g., when the initial culture density increased to 0.3 g/l, *Chlorella* sp. cells could grow well with 100 ppm SO<sub>2</sub> and 300 ppm NO [45,53,86,91,92]. Additionally, for some microalgal species, the short lag phase and steep log phase could be observed with a high initial concentration [60]. However, increasing initial concentration can intensify the competition among microalgae for nutrients uptake, light, and other conditioning factors when they are insufficient. In contrast, high initial biomass concentration increases the carbon fixation and biomass production while nutrients source and light conditions are sufficient. In addition, it should be noted that initial biomass concentration usually has an interactive influence on the microalgal growth with other conditioning factors such as C source, N source, light intensity and temperature, which are decisive to the special growth characteristics. Therefore, there is a complex relationship between initial inoculation density and special growth.

#### 4.4. Culture temperature

As expected, culture temperature is an important conditioning factor to microalgal-CO<sub>2</sub> biofixation and biomass production because microalgal photosynthesis is naturally a series of temperature-dependent physicochemical reaction processes. Generally, the effect of temperature on microalgal growth can be evaluated by a quasi-parabola opening down. The low temperature is not in favor of enhancing the activity of Rubisco, thereby the process of photosynthesis and CCM will not be accelerated; while the extremely high temperature inhibits the microalgal metabolic behavior and respiration intensity [93], and also causes low CO<sub>2</sub> solubility in water according to Henry's law. Therefore, there is an optimal temperature value or range for microalgal growth. According to previous research results, most commonly microalgal species can tolerate temperatures between 15 and 26 °C [9]. The optimum temperature for microalgae varies with microalgal species and culture medium composition. An intermediate value of 18–20 °C close to room temperature was often recommended due to high growth rates under that. Moreover, the microalgal growth would be inhibited or the lag phase would be lengthened for most microalgal species when the culture temperature is far higher more than their optimal growth temperature [68,74].

Usually, temperatures lower than 16 °C will slow down microalgal growth, whereas those higher than 35 °C are usually lethal for a number of microalgal species. However, the tolerance and adaptability of some microalgae to high temperature can be improved by the induced acclimation technology, e.g., the domesticated species *Chlorella* sp. T-1 had an optimal growth temperature of 35 °C [42] while *Chlorella* KR-1 [74] and ZY-1 [55] were able to grow at the temperature up to 40 °C, and even with high special growth rate.

#### 4.5. Light

For the microalgal biofixation of CO<sub>2</sub> from combustion flue gas, the light source can be usually divided into natural sunlight which is applied in both open and closed cultivation, and artificial cold light which is mainly applied in closed cultivation. No matter what type of light source, light is the most influencing factor to microalgal carbon sequestration and biomass production because of the photoautotrophic characteristics of microalgae. Usually, the effect of light is presented in two ways: light intensity and light-dark periods and cycles.

There is complex relationship between light intensity and microalgal growth. In the light-limited area, photosynthesis rate increases as light intensity increased. Regarding the light intensity as only single factor, its effect on special growth rate for microalgae can be described by the following semi-empirical model:

$$\mu = \mu_{\max} I^n / (I^n + K_I^n) \quad (3a)$$

$$\mu = \mu_{\max} I / (I^2 + I + K_I) \quad (3b)$$

where  $K_I$  is half-saturation constant for light intensity ( $\mu\text{E}/\text{m}^2/\text{s}$ ).

With continuous increase of light intensity, microalgal photosynthesis has an increasing rate but a gradually reduced acceleration. Light intensity at maximum photosynthesis rate is called the saturated light intensity after that the light-saturated area is reached. After light-saturated area photosynthesis can be weakened and inhibited with increased light intensity (also called photoinhibition). Similarly, the minimum limit of the light-limited area is called as compensated light intensity. It should be noted that the light-limited range also varies with microalgal species [74]. The most often employed light intensities range between 100 and 200  $\mu\text{E}/\text{m}^2/\text{s}$ . In addition, the effect of light intensity on microalgal growth must take into account the interactions between the various influencing factors, e.g., culture temperature is able to adjust the required light intensity by affecting the metabolic reaction of microalgal cells. Specifically, under higher culture temperature microalgae may well grow with lower light intensity requirement. Microalgal photosynthesis can also be enhanced as the nutrient concentrations increased under high light intensity while it can be weakened when the cell density (biomass) increased under low light intensity.

Besides light intensity, it was found that light-dark periods and cycles could also influence the microalgal growth significantly [94]. The light-dark periods for most microalgal cultivation include 24 h:0 h (Although some microalgal species do not grow well under constant illumination), 16 h:8 h and 12 h:12 h. For a specified microalgal species, there are different growth characteristics under different light-dark periods. The experiment indicated that the photosynthetic efficiency could be decreased when the dark period was up to 50% of the cycle period (12 h:12 h) [14]. Moreover, due to the difference of photobioreactor configuration, the light distribution and light-dark cycle are also influenced by fluid-cell flow and inter-cell absorption and scattering to light, resulting in effects on the whole processes of microalgal CCM and photosynthesis [95].

#### 4.6. Nutrients

Besides trace metals and vitamins, N and P are the two most important nutrients in the culture medium to maintain the microalgal growth. As a constituent of both nucleic acids and proteins, nitrogen is directly associated with the primary metabolism of microalgae [9]. Usually, in the culture medium for microalgal cultivation, nitrogen sources exist in the forms of nitrate ( $\text{NO}_3^-$ ), nitrite ( $\text{NO}_2^-$ ) and ammonia salt such as urea ( $\text{NH}_4^+$ ); while phosphorus exists in the forms of hydrogen phosphate



( $\text{HPO}_4^{2-}$ ) and dihydric phosphate ( $\text{H}_2\text{PO}_4^-$ ). Appropriate concentrations of N and P are able to effectively promote the microalgal growth. As expected, extremely low N and P concentrations would cause the microalgal growth inhibition while high N and P concentration would present toxic effects on microalgae, decreasing their growth rate and even causing death of them.

The effects of N and P on the microalgal growth as well as carbon fixation and biomass production are mainly attributed to the types of nitrogen source in addition to N concentration. When culturing *Isochrysis galbana* in nitrate, nitrite and urea medium, it was found that urea cultures showed significantly higher growth rate as well as more lipids than nitrate and nitrite medium which presented very similar trends with low growth rate [48]. In addition, high N/P ratio is helpful to increase the growth rate and biomass production under conditions of atmospheric  $\text{CO}_2$  as the carbon source. Moreover, it should be noted that the N source has the interactive influence with other process factors particularly with the C source [96].

#### 4.7. pH value

According to the microalgal CCM, most important DIC forms,  $\text{CO}_2$  and  $\text{HCO}_3^-$ , are closely related to the pH value in the culture medium [58,59] as there are reversible chemical equilibriums. Besides chemical properties of culture medium, pH change in medium is attributed to the hydrolysis of  $\text{CO}_2$  and water-soluble pollutants such as  $\text{SO}_2$  from flue gas. Effects of pH on microalgal-carbon biofixation and biomass production mainly depend upon  $\text{CO}_2$  and  $\text{SO}_2$  concentration.

For atmospheric  $\text{CO}_2$ , there is no significant pH change in the culture medium. The pH ranges are about 7.9–8.3 for marine water and about 6.0–8.0 for freshwater. Because the  $\text{CO}_2$  concentration in air is extremely low (0.038%),  $\text{CO}_2$  uptake by microalgal cells can cause pH rising to more than 9.5–10 in this situation. However, for post-combustion flue gas, pH sharply reduced to about 5.5 as  $\text{CO}_2$  has a high concentration of 10–20% or more. Additionally, 100–250 ppm  $\text{SO}_2$  also makes the pH value in the flue gas reduced to about 3.5–2.5 at aeration rate of 0.25 vvm. Usually, low pH has an inhibited effect on Rubisco activity in the CCM, leading to the inhibition to microalgal growth. Most microalgal species have their own optimal pH ranges to grow (e.g., *Synechococcus* PCC7942 at pH 6.8 [97]). However, after habituated culture some microalgal species may be tolerated to extremely low pH values (e.g., *Chlorella* sp. KR-1 at pH below 4.0 [74]).

### 5. Effects of hydrodynamic process

#### 5.1. Flow and mixing

Microalgal culture modes usually included the open (e.g., raceway ponds, lake, etc.) and closed cultivation (e.g., column, tubular and flat plate, etc.). Regardless of the microalgal photobioreactor (PBR) types used in these culture modes, appropriate turbulent flow and mixing in gas–liquid–solid ( $\text{CO}_2$ -medium-microalgae) phases are necessary and important to enhance mass transfer, to achieve light, temperature and nutrients equalization, to remove produced oxygen and to prevent the microalgal aggregation and sedimentation. However, excessive turbulent flow and mixing may lead to damage to microalgal cell because not all microalgal species can tolerate vigorous shear stress caused by flow turbulence.

Besides the jet pumping for open culture system, methods of flow and mixing in a microalgal PBR for closed culture system usually include mechanical stirring and gas aerating. For mechanical stirring, the effect of flow and mixing is directly associated

with stirring speed. Especially, shear stress near the impeller has a maximum value which may cause a larger damage to microalgal cells. Currently, as a most widely used method, gas aerating (usually using bubbling) is able to provide a relatively good flow and mixing performance. Aeration rate is an important parameter besides the bubble size in the gas aerating method. It is defined as the gas volumetric flow rate per unit volumetric culture medium (vvm). As expected, an appropriate turbulence effect by an appropriate aeration rate is helpful to increase the microalgal performance on carbon fixation and biomass production, but extremely high aeration rate also gives rise to increase of shear stress especially in the processes of bubble generation, bubble deformation (e.g. bubble coalescence and break-up) and gas–liquid interface formation [98–100]. Moreover, the flow pattern by aeration can be improved using optimized PBR configuration, such as using horizontal and vertical baffles in flat plate airlift. [101]. Also, the turbulent mixing by aeration can be controlled via adequate use of baffles [9]. Recently, there were preliminary investigations using a computation fluid dynamics (CFD) technique to optimize the flow and mixing in PBR [102–104].

Usually, performance on microalgal- $\text{CO}_2$  fixation and biomass production was found to have a nonlinear relationship with aeration rate. For most closed cultivation, the recommended aeration rate is 0.10–1.00. The optimum aeration rate varies with microalgal species and PBR configuration, e.g., 0.025–1 vvm was proposed to be cost-effective for 5% or 10% (v/v)  $\text{CO}_2$  aeration and 0.05 vvm for a flat-panel PBR [105]. Moreover, investigation indicates that the aeration strategy has an influence, e.g., gradual increase of  $\text{CO}_2$  supply could enhance the growth rate and  $\text{CO}_2$  fixation rate compared with constant  $\text{CO}_2$  supply. This is because microalgae could adapt to the new  $\text{CO}_2$  concentration well and enhance their  $\text{CO}_2$  tolerance when  $\text{CO}_2$  supply slowly increases, especially under a relatively higher concentration of  $\text{CO}_2$  [46].

#### 5.2. Mass transfer

There is a complex mass transfer process in a Microalgal-PBR. It involves a process of three-phase mass transfer contains mass transfer between: gas ( $\text{CO}_2$ )–liquid (medium), gas ( $\text{CO}_2$ )–solid (microalgae), and liquid (medium)–solid (microalgae). In the gas aerating method, mass transfer performance and biochemical reaction rate depend on bubble size, gas hold-up, gas–liquid contact area and  $\text{CO}_2$  concentration and gas/liquid ratio, etc. In recent years, some new methods were used to improve mass transfer drive, including enhancing  $\text{CO}_2$  concentration gradient (e.g., using  $\text{NaHCO}_3$  as additive to generate chemical reaction), or expanding contact area (e.g., using hollow-fiber membrane PBR [106,107]).

$\text{CO}_2$ -medium mass transfer process is usually regarded as a gas–liquid absorption process. According to governing equations based on the two-film theory, mass transfer rate can be expressed as  $dC_{\text{CO}_2}/dt = k_l a (C_{\text{CO}_2}^* - C_{\text{CO}_2})$ , where  $k_l$  is the mass transfer coefficient based on liquid phase,  $a$  is the specific area, and  $C_{\text{CO}_2}^*$  and  $C_{\text{CO}_2}$  are the  $\text{CO}_2$  concentration at saturation status and in the culture medium, respectively. The mass transfer coefficient  $k_l a$  is a function of microalgal bio-characteristics and operating conditions. Several novel theoretical equations have been developed to model the mass transfer between  $\text{CO}_2$  and microalgae, e.g., linking the overall volumetric gas–liquid mass transfer coefficient with the gas holdup and the superficial aeration velocity and other principal operation variables [108], or using a nonequilibrium mathematical model of  $\text{CO}_2$  dynamics considering the hydration of dissolved  $\text{CO}_2$  to bicarbonate ion ( $\text{HCO}_3^-$ ) as well as the uptake and/or cycling [109], etc.

As a most important parameter characterizing mass transfer,  $\text{CO}_2$  removal efficiency was also used to evaluate the microalgal- $\text{CO}_2$  fixation performance in a PBR in addition to the mass transfer



coefficient. It can be determined or calculated by the difference of the CO<sub>2</sub> concentration between the influent and effluent gas of a PBR. Experiments showed that a PBR could reach to higher CO<sub>2</sub> removal efficiency if the high-performance microalgal species were used under optimized operating conditions, e.g., for microalgae *Chlorella* sp. at CO<sub>2</sub> concentrations of 2%, 5%, 10% and 15% (v/v), the CO<sub>2</sub> removal efficiency was 58%, 27%, 20% and 16%, respectively [60]. Other microalgal species, *S. obliquus* WUST4 can adapt to the acural flue gas and reached to the CO<sub>2</sub> removal efficiency of 67% under 12,000–13,000 lx light intensity, 12% CO<sub>2</sub> concentration and 0.1 vvm aeration rate [110].

## 6. Process improvement and application

Over the past two decades, microalgae-based CO<sub>2</sub> fixation, biomass production and its energy utilization have made great progress in both bench-scale scientific research and pilot-scale application [111–113]. Currently, more than 50 institutions in the world are committing to commercialization of microalgal technology and products. Details of the startup companies are available in Ref. [114–116]. They are distributed in the America (~66%), Europe (~14%), Asia (~16%) and others (~4%). Volumes and sizes of some photobioreactors (PBRs) for laboratory-scale microalgal-CO<sub>2</sub> fixation and biomass production were listed in Table 1. The features (pros and cons) of PBRs for large-scale industrial application were summarized and compared according to their structure and technical-economic performance [117,116,14].

Process improvement as a middle measure is important to ensure microalgal-CO<sub>2</sub> fixation and biomass production more efficiently. Whether bench-scale research or pilot-scale application, performances of carbon fixation and biomass production highly depend on the process conditions and parameters. For the bench-scale research, the selection, cultivation and promotion for high-performance microalgae species may be one of the important goals. Besides, the performance evaluation of microalgae under the harsh process parameters and environmental factors (e.g., high CO<sub>2</sub> concentration, high temperature and toxic pollutants in flue gas) is also needed to be determined by laboratory research. For the pilot-scale application, microalgal cultivation is mainly affected by the culture temperature, light exposure and hydrodynamic conditions. Compared to closed cultivation, open cultivation is more sensitive to and influenced more significantly by these factors, e.g., the outdoor temperature and light intensity variation in day–night and different season have more adversely influence on microalgal growth.

Usually, the open microalgal cultivation includes shallow, mixed and raceway ponds. They have the advantages of extremely simple construction, low-cost operation and easy maintenance. The open ponds are designed as 0.25 m in width and 0.2–0.5 ha in area for commercial microalgae production [118,119]. However, due to the limitation of light penetration they are unable to be designed with large depth, usually 0.15–0.35 m and maximum 0.4 m in depth in order to ensure the light exposure to microalgal cells. Considering the economic effect, the open ponds are usually lined with cement. In some cases, plastic materials were used to enhance light exposure, minimize the effect of temperature fluctuation and prevent microalgae from cross contamination. Moreover, the open pond can be also installed with paddle wheel in practice, which actually could enhance the process parameters such as turbulence mixing and mass transfer.

Another kind of high rate pilot-scale microalgae production is closed cultivation, including cultivation using tubular, bubble column and air-lift, and flat plate PBRs. No matter what kind of design, the improvements of process parameter for CO<sub>2</sub> fixation and biomass production are mainly focused on physicochemical parameters, e.g., light exposure and nutrition conditions, and

hydrodynamic parameters including mixing and mass transfer by increasing the gas–liquid contact area and retention time, although there is still controversies in the economy and practicality when they are scaled up for commercial use [120]. Specifically, for the tubular PBRs, the diameter was designed to be about 5 cm for small scale and 10–20 cm for large scale. As expected, decreased diameter and right position (e.g., horizontal or vertical position) help improve the light exposure [121]. For the purpose of high concentration culture, tubular PBRs need to be scaled-up by means of increasing the tube length and diameter. However, increase of length may give rise to the nonuniformity of CO<sub>2</sub> mass transfer and accumulation of dissolved oxygen, and increase of diameter results in an adverse effect on the light characteristics [122]. In comparison, using multiple parallel-tube configurations and increasing the tube unit number without increasing diameter may be more acceptable measures to improve light exposure and mass transfer. Compared with tubular PBRs, PBRs using bubble column design were considered to be competitive in technical-economic performance. Bubble column PBRs can be designed as more than 2–5 m in height and 50 cm in sectional dimension with rounded or rectangular cross-sections. A vertical orientation is helpful to save land area and reduce energy consumption, making it easy to scale-up. Additionally, it has a wide adaptability to light intensity and superficial gas velocity, making it easy to operate. Given the physicochemical parameters, improvement of key operating parameters including appropriate increase of gas hold-up and decrease of bubble diameter, are in favor of enhancing their turbulence and mass transfer performance in gas (CO<sub>2</sub>)–liquid (culture medium)–solid (microalgae cell). In practice, bubble columns can also be designed as multistage or series connection to obtain high CO<sub>2</sub> fixation and biomass productivity. As other vertical PBRs, air-lift PBRs are also considered to have an improvement on gas–liquid mixture and light/dark cycle. However, the potential risk in microalgal cell damage due to high shear effect should be avoided. Flat panel was considered as another kind of closed microalgae cultivation system for large scale application. They are usually featured with large surface area and vertically suspended orientation, which effectively increase the surface area illuminated by both direct and diffuse light and provide structural support and even temperature control to optimize microalgal growth [123–125,94]. CO<sub>2</sub> fixation and biomass production can be improved using high aeration rate to accomplish turbulence mixing, CO<sub>2</sub> mass transfer and removal of excess oxygen in the culture medium [105]. However, this configuration still would be challenging due to the high stress to microalgal cell and high operating cost. In addition, some other else special PBRs were also used in practice, e.g., a tower PBR is able to achieve CO<sub>2</sub> fixation and biomass production from combustion flue gas [114]. This structure increases the gas–liquid contact area and retention time using multi-layer design and keeps constant light intensity using a built-in light source.

Overall, microalgae-based CO<sub>2</sub> fixation and biomass production in practice are also influenced by multiple process factors including microalgal species, physicochemical and hydrodynamic conditions as mentioned above. Therefore, to maximize the performance on CO<sub>2</sub> fixation and biomass production, the synergistic effect and global optimization (optimization of PBR design is essentially included in the process parameter optimization) of process parameters are important issues and still required to be solved when using microalgae-based CO<sub>2</sub> fixation and biomass production in the industrial fields.

## 7. Conclusions and prospects

Recent progresses on process effect of CO<sub>2</sub> fixation and biomass production using microalgae were summarized and reviewed, with

focusing on microalgal species, physicochemical and hydrodynamic process conditions. On the whole, the microalgal-based CO<sub>2</sub> biofixation and biomass production has broad prospects for development. But the following issues still need to be solved in the future.

The selection and cultivation of energy microalgal species: Most of microalgae which are suitable for sequestration of CO<sub>2</sub> from flue gas are the single-cell microalgae especially on *Chlorophyta*. They have high growth rate and strong environmental adaptability, such as good endurance to high CO<sub>2</sub> concentrations, high temperature and low pH value. However, most of them were selected and separated on the basis of bench-scale domestication. They are hardly to be used for pilot-scale cultivation and CO<sub>2</sub> fixation. Therefore, selection and cultivation of the nature microalgal species, which are more suitable for large-scale sequestration of CO<sub>2</sub> from actual combustion flue gas, is still required in the future.

Mechanism of action and interactive influence of multiple process factors: Usually, most of the physicochemical and hydrodynamic process parameters have important nonlinear effects on microalgal growth and its carbon sequestration performance. However, their detailed mechanism of action, especially the impact on the activity of carbonic anhydrase (CA) and regulation and control of CO<sub>2</sub> concentrating mechanism (CCM) have not yet been completely revealed and still need to be explored. Additionally, for microalgal growth and carbon sequestration, it is important to comprehensively consider the effects of all process factors. Previous studies mainly focused on the independent effect of the single factor or interactive effect of two factors (C and N) interactive effect. Up to now there are few investigations involving the comprehensive relationship between microalgal CO<sub>2</sub> fixation/biomass production kinetics and process parameters. The related issues about multi-objective optimization are also rarely reported.

CFD-based PBR design and process conditions optimization: Despite the different photobioreactor geometries and configurations used in open and closed type cultivation, they are essentially similar because they are both used to intensify the mass transfer and the photosynthesis between the microalgal cells and the outside environment. To mathematically model these processes, some new theories and technologies, e.g., CFD model coupled with mass transfer model, chemical reaction and equilibrium model, light attenuation model and new membrane theory, are worth to be further developed to design the photobioreactor geometry and optimize the operating conditions, in order to improve CO<sub>2</sub> fixation and biomass production performance for microalgae.

Resourcelization and energy utilization of microalgal biomass product: It is important to use the microalgal product as biofuel after carbon biofixation due to the situation of global energy crisis. With the development of new efficient and economical conversion technology, microalgal energization including liquid extraction and co-gasification will have a broad developing prospect. It will be helpful to realize the dual objective including both emission reduction of CO<sub>2</sub> and reuse of biomass product.

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